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Research Article

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Appraisal of heavy metal contents in soils using different digestion methods

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Abstract The concentration of some heavy metals (Fe, Cu, Zn, Cr, Pb, Ni, Cd) were analysed in soils in and around Keteren-Gwari Mechanic village, Minna metropolis, Niger State, North-central Nigeria using Atomic Absorption Spectroscopy (AAS) (Buck Scientific 210VGB). Two digestion methods were used to concentrate the metals. Mean concentration for Fe was 6548±72.94µg/g; 24.57±16.74µg/g Cu; 24.57±16.74µg/g Zn; 11.64±9.02µg/g Cr and BDL for Pb, Ni and Cd using aqua-regia digestion while mean concentrations using $HClO_4$, HNO_3 and H_2SO_4 mixture digestion were 5175±29.99µg/g Fe; 27.07±17.43 µg/g Cu; 126.57±97.29 µg/g Zn; 18.14±12.45 µg/g Cr; 128±22.22 µg/g Pb and BDL for Ni and Cd. The contamination factor (CF) calculated was shown to be Fe > Zn > Cu > Cr for surrounding soil samples and Fe > Pb > Zn > Cu > Cr in the mechanic village work area. It is recommended that laws are formulated and enforced that prevent any form of farming in the area, mechanic villages be relocated out of the city and other environmental protection regulations to stop the build-up of these metals in similar locations be implemented.

Keywords Heavy metals, Mechanic villages, Minna, Pollution

Introduction

With a land area of approximately 950,000 km^2, Nigeria is richly endowed with diverse metal and non-metal resources. However, there are staggering environmental problems manifested in various forms to present a grim of woes across the lengths and breadth of the nation. Heavy metal pollution with other types of degradation such as erosion, loss of fertility and the continuing speed of urbanization are major threats to the sustainability of the safe environmental resources in Nigeria [1].

Foremost amongst the modes of ecosystem contamination in urban areas according to Adewole and Uchegbu (2005) [2] is the prevalence of automobile workshops and service stations. Automobile wastes include solvents, paints, hydraulic fluids, lubricants and stripped oil sludge;all results of activities such as battery charging, welding and soldering, automobile body works engine servicing and combustion processes [3-4]. All these find their way somehow into the ecosystem especially the aquatic habitat. The significant contamination of seeds, plants and plant products with toxic chemical elements due to contaminated soil and water has been observed as a result of these toxicants into the sea, rivers and even irrigation channels. Afterwards, the consumption of contaminated vegetables constitutes an important route of animal and human exposure.

In Nigeria, automobile workshops are concentrated in areas known as “mechanic villages” [5]. These are places officially designated for repairs and servicing of motor vehicles by the government. Although mechanic villages are laudable in that they save automobile owners’ the trouble of searching for mechanic specialists, prevent motorists from falling into the hands of incompetent mechanics and create an opportunity for knowledge sharing among artisans and mechanics, their locations and indiscriminate practices make them a cause of worry and reason for constant monitoring. Accumulation of heavy metals from automobile workshops deteriorates vegetation that is nearby, accumulate in plant tissues, deteriorate surface runoff and percolate the water table causing non-point pollution [4]. Microbes in the soil used in bioremediation are also destroyed.

In developing countries, environmental laws are rarely observed and so industrial growth and its associated environmental problems such as soil, plant and water is constantly increasing [6]. The problem of environmental pollution due to toxic metal has begun to cause concern now in most major metropolitan cities [7]. Unlike energy which tends to deplete and become dispersed at each trophic level, heavy metals become more concentrated with each trophic level within the food chain; this is referred to as bioaccumulation [8].

Data on the heavy metal levels in and around mechanic Villages especially in Niger State, Nigeria is scarce in literature. Adverse effects are supposed, when the concentration of heavy metals exceed the permissible limits in soils. This study therefore, is to assess the levels of Fe, Cu, Zn, Cr, Pb, Ni and Cd in Soils in and around Keteren-Gwari mechanic village, Minna metropolis, Niger State.

Materials and Methods

Study Area

The study area is the mechanic village at Keteren-Gwari, Minna metropolis of Niger State. Minna is located within Latitude 9° 36´ 50´N and Longitude 6° 33´ 25° E covering a land area of 88$Km^2$and has a population of about 202,151 at the 2006 census (National Populations Commission). The area is characterized by high temperatures of about 29°C-31°C; the climate presents two distinct seasons: rainy season (Apr-Oct) and dry season (Nov-Mar) [9].

Sample collection

Composite Soil samples were collected at depths of 0-15cm and 15-30cm from randomly selected points within the Mechanic Village. A total of four composite samples were collected from the mechanic village work area (P1, P2, P3 & P4) while two composite samples were collected from the surrounding areas (F1 & F2) into clean polythene bags. Samples were then air dried for 48 hours, ground and sieved using 0.5mm mesh size sieve to have uniform particles. Control sample was also collected at a neutral location about 5 km away from the site.

Sample Preparation and Analysis

Soil samples were prepared using two digestion methods.

***First Procedure*:** Homogenized samples of 2.0g were each measured into 250cm^3 glass beakers and 8cm^3 of freshly-prepared aqua-regia (3:1 HCl and HNO_3) added. The mixture was then heated at 200ºC on a hot plate for 2hrs. After evaporation to near dryness, the sample was then dissolved with 10$cm^3$of 2% nitric acid and filtered through Whatman filter paper before being diluted with deionised water to mark [7].

***Second Procedure*:** 1g of ground samples in each case was placed in a 100cm^3 flask. 2$cm^3$of 70% perchloric acid ($HClO_4$) was added followed by 10cm^3 concentrated nitric acid (HNO_3) and 1cm^3 sulphuric acids (H_2SO_4). The mixtures obtained were then heated till dense white fumes appeared before being further heated for 15 minutes. The mixtures were then filtered through Whatman filter paper and made to mark with distilled water. Blank and control samples were also prepared in the same manner for instrumental analysis.

Aliquots of the diluted solution were analysed for heavy metals, using Atomic Absorption Spectrophotometer (AAS) (Buck Scientific model 210VGP). All analysis was performed in triplicates.

Results and Discussion

The results of the analysis are presented in tables 1 and 2. A broad view of the results showed a variation in the concentration of metal ions in all samples and across digestion methods used.

for aqua-regia and H_2SO_4, HNO_3 and $HClO_4$ mixture digestions respectively. Minimum values from both digestion methods of 2931±11.31μg/g and 3568±4.9μg/g for Aqua-regia and H_2SO_4, HNO_3 and $HClO_4$ mixture digestion respectively where far greater than the concentration of control samples of 32±1.41μg/g and 35±2.83μg/g in same order. This implied very high Fe contamination. Mean concentration for Fe showed better recovery for samples digested using aqua-regia than H_2SO_4, HNO_3 and $HClO_4$ mixture. Within samples, Fe was higher in samples P1 and P2 which were from the mechanic village work area while F1 and F2 collected from the surrounding had lower Fe concentrations in both digestion methods used. This could be attributed to automobile activities like panel beating and body works done in the work area and then absorption of metals by vegetables grown in the surrounding farm area.

Table 1: Heavy metal concentration in Soil digested with aqua-regia (µg/g)

Sample	Fe	Cu	Zn	Cr	Pb	Ni	Cd
P1	9819±11.30[a]	43.50±1.41[d]	160.50±2.83[d]	11.00±0.71[bc]	BDL	BDL	BDL
P2	8690±14.14[a]	55.00±4.24[e]	231.50±1.41[f]	13.50±1.41[c]	BDL	BDL	BDL
P3	3892±26.16[a]	17.00±1.41[c]	198.5±11.31[d]	6.50±1..41[ab]	BDL	BDL	BDL
P4	2931±11.31[a]	11.50±1.41[c]	68.75±4.24[c]	6.50±1.41[ab]	BDL	BDL	BDL
F1	4265±21.21[a]	16.25±0.04[bc]	40.00±2.83[b]	7.50±0.71[ab]	BDL	BDL	BDL
F2	3058±11.30[a]	11.25±0.03[a]	42.50±2.12[b]	5.00±0.71[a]	BDL	BDL	BDL
Mean	6548±72.94	24.57±16.74	24.57±16.74	11.64±9.02	BDL	BDL	BDL
Control	32±1.41[a]	17.50±2.12[c]	26.00±2.83[a]	31.50±4.95[d]	BDL	BDL	BDL

P1, P2, P3 & P4 = soil samples collected from mechanic village work area
F1 & F2 = soil samples collected around mechanic village
a,b,c,d=significant difference BDL=below detection limit

Table 2: Heavy metal concentration in Soil digested with Soil H_2SO_4, HNO_3, $HClO_4$ (µg/g)

Sample	Fe	Cu	Zn	Cr	Pb	Ni	Cd
P1	9006±36.77[g]	49.00±5.67[d]	153.50±10.60[c]	12.00±0.71[a]	639±21.21[d]	BDL	BDL
P2	8846±28.28[f]	53.00±4.24[d]	274.00±31.11[d]	14.00±2.83[a]	143±28.28[c]	BDL	BDL
P3	4347±9.89[c]	15.00±1.41[ab]	245.00±5.65[d]	12.00±0.00[a]	64±4.24[b]	BDL	BDL
P4	4655±4.95[d]	14.00±2.83[ab]	99.00±9.89[b]	14.00±1.41[a]	47±9.89[b]	BDL	BDL
F1	5768±9.89[e]	19.00±1.41[b]	45.00±2.83[a]	16.00±1.41[a]	BDL[a]	BDL	BDL
F2	3568±4.95[b]	7.50±2.12[a]	43.00±2.83a	12.00±1.41[a]	BDL[a]	BDL	BDL
Mean	5175±29.99	27.07±17.43	126.57±97.29	18.14±12.45	128±22.22	BDL	BDL
Control	35±2.83[a]	32.00±1.41[c]	26.50±4.24[a]	47.00±5.66[b]	3.1±0.28[a]	BDL	BDL

P1, P2, P3 & P4 = soil samples collected from mechanic village work area
F1 & F2 = soil samples collected around mechanic villages
a, b, c, d=significant difference BDL=below detection limit

Iron was largely present in all soil samples analysed with mean concentrations of 6548±72.94 and 5175±29.99µg/g Copper concentrations from tables for samples digested with aqua-regia was 24.57µg/g with control samples having a mean concentration of 17.5±2.12µg/g. Concentrations obtained from surrounding soils F1 and F2 were also lower compared to those of the mechanic work area with significant variation between results at ($P \leq 0.05$). Similarly, mean concentrations of Cu from table 2 for H_2SO_4, HNO_3 and $HClO_4$ mixture digestion was 27.07µg/g with control samples giving a mean concentration of 32±1.43µg/g. Better recovery was observed for Cu using H_2SO_4, HNO_3 and $HClO_4$ mixture as compared to aqua-regia. Generally, the data shows that Cu levels were higher in the mechanic work area than in its surroundings. The distribution levels around the mechanic work area also differed depending on the type of automobile repair conducted at each station. Results obtained are however below the permissible limits set by Malaysia for soils 140mg/Kg [10] and other countries Australia(100mg/Kg), Canada (100mg/Kg), Poland (100mg/Kg), Japan (125mg/Kg) and Great Britain (100mg/Kg). Some values however exceeded that for Germany (50mg/Kg) [3].

The mean concentration for Zinc from tables 1 and 2 showed that values for aqua-regia digestion was 109.6±81.71µg/g while for the later digestion was 126.57±97.29 indicating that H_2SO_4,HNO_3 and $HClO_4$ mixture gave a better recovery in most cases. Zinc concentrations in all soil samples were greater than those of control samples with a mean value of 26.25µg/g indicating elevated levels of Zn. For aqua-regia digestion, lowest values were obtained in the farm samples F1 and F2 with concentrations of 40±0.04µg/g and 42.50±2.12µg/g respectively. The highest value was from the work area P2 with value of 231.50±1.41µ/g. Similarly, H_2SO_4, HNO_3 and $HClO_4$

mixture showed that lowest values were from the farm samples F1 and F2 with concentrations of 45±2.83µg/g and 43.0±2.83µg/g respectively and maximum value from work area P2 with concentration of 274±31.11µg/g. This trend could be attributed to the absorption of Zn from the farm soils by vegetables grown on them. Values obtained in the present study were higher than those from the control sites which were 26.00±2.83µg/g for aqua-regia and H_2SO_4, HNO_3 and $HClO_4$ mixture respectively indicating anthropogenic sources of pollution [3, 5]. All values obtained were below maximum permissible limit of 300mg/l set by WHO (2003).

Chromium levels using aqua-regia digestion was 11.64±9.02µg/g and 18.14±12.45 µg/g for samples digested using H_2SO_4, HNO_3 and $HClO_4$ mixture with significant variation in sample concentration at $P \leq 0.05$. From the results it is observed that aqua-regia had a better recovery for Cr than the former. It is reported that Chromium (III) and (VI) inhibit the activity of soil enzymes like dehydrogenase, urease and phosphatase and alkaline phosphatise [11]. Concentration of Cr in this study did not exceed the limit set by the United Kingdom of 300µg/g and 100mg/l by WHO [12].

Lead is noticed to be below detectable limits using aqua-regia digestion while in H_2SO_4, HNO_3 and $HClO_4$ digestion, values ranged from BDL for farm samples F1 and F2 to a maximum value of 639±21.21µg/g. Mean Pb concentration from table 4.4 was 128±22.22µg/g and suggests a better recovery of Pb using the H_2SO_4, HNO_3 and $HClO_4$ digestion method compared to the former. The absence of Pb in samples F1 and F2 which are farm samples might suggest continuous cropping as a cause of removal of Pb from the soils to a minimum level. Soil Pb concentrations greater than 1.0 mg/Kg generally indicate a local source of pollution [13]. In all results however, only samples P1 and P2 were above maximum allowable limits set by Australia (100µg/g), Poland (100µg/g), and United Kingdom (100µg/g) while only sample P2 was greater than the allowable limit set by Germany (500µg/g) [14].

Nickel and Cadmium were below detection limits for both aqua-regia digestion and H_2SO_4, HNO_3 and $HClO_4$ mixture digestion methods. Reason for this might be due to the type of automobile repair activity occurring in the sampled sites which are mainly panel-beating whereas Cd accumulates mainly from battery charging [15], car pigments & painting [16] and soldering. Ni is known to accumulate in plants and with intake of too large quantities of Ni from plants grown in Ni rich soils; there are also higher chances of developing cancers of the lung, nose larynx and prostate as well as respiratory failures, birth defects and heart disorders. Maximum allowable limits for Cd is 3.00µg/g while that for Ni content in soil is 75µg/g [10].

Contamination Factor (CF)

CF indicates the metal enrichment in the soil [17]. It is the ratio obtained by dividing the mean concentration of each metal in the soil by the baseline or background value (concentration in non-polluted soil) [18]. CF parameter is expressed as follows

$$CF = \frac{Cmetal}{Cbackground}$$

Where CF = Contamination factor

C_{metal} = Concentration of polluted sample

$C_{back\ ground}$ = Concentration of background value

Background value for metal in Nigerian soils is unavailable [19] and so values from control site was used to estimate contamination factor. Interpretations for results are represented as CF < 1 indicates low contamination, $1 \leq CF \leq 3$ indicates moderate contamination, $3 \leq CF \leq 6$ indicates considerable contamination and CF > 6 indicates very high contamination.

From Table 3, CF for Fe ranged from 91.7 to 306.8 and those for Pb ranged from 15.16 to 206.1 which suggest very high contamination. CF for Zn ranged from 1.5 to 1.7 for samples F1 and F2 which indicates moderate contamination while a range of 2.6 to 10.3 was recorded for samples P1 to P4. Low contamination was recorded for Cu in all samples except P1 and P2 which were moderately contaminated with values ranging from 1.5 to 3.1. All values for Cr were less than 1 which shows very low contamination. The degree of contamination in decreasing order is shown to be Fe > Zn > Cu > Cr for surrounding soil samples and Fe > Pb > Zn > Cu > Cr in the mechanic village work area. This pattern corresponds to results obtained by Usman *et al.*, (2013) from mechanic villages in North-central Nigeria and Ekpo *et al.*, (2013) from Cross-river Nigeria.

Table 3: Contamination factor for soils

Sample	Fe	Cu	Zn	Cr	Pb	Cd	Ni
P1 A	306.8	2.6	6.2	0.35	-	-	-
B	257.3	1.5	5.8	0.26	206.1	-	-
P2 A	271.6	3.1	8.9	0.42	-	-	-
B	252.7	1.7	10.3	0.3	46.12	-	-
P3 A	121.6	0.97	7.6	0.21	-	-	-
B	124.2	0.5	9.2	0.26	20.7	-	-
P4 A	91.7	0.65	2.6	0.21	-	-	-
B	133	0.43	3.7	0.3	15.16	-	-
F1 A	133.3	0.9	1.5	0.24	-	-	-
B	164.8	0.6	1.7	0.34	-	-	-
F2 A	95.58	0.64	1.6	0.16	-	-	-
B	101.95	0.23	1.6	0.26	-	-	-

(A-Aqua regia digestion, B-H_2SO_4 digestion)

Conclusions and Recommendations

Soil samples from the mechanic village work are more contaminated with heavy metals than those collected from the surrounding areas; this confirms that sources of pollution are anthropogenic in nature. However, the distribution pattern of the heavy metal on both sides of the mechanic village confirms the effect of the mechanic activities on its surrounding and host areas. This raises significant concern for safety of the environment and health impacts on humans, animals and vegetation. It is recommended that Mechanic workshops situated within the metropolis should have their floors well cemented or cast with proper drainages used for automobile wastes especially oils, lubricants and spilled gasoline; Recycling processes should be considered whereby used oils and lubricants are re-processed chemically to extract the heavy metals from them and harness them for other uses under safe best practices. Also, auto mechanics should be educated on proper waste disposal in mechanic villages/workshops and how to practice safe handling of all generated waste to safeguard their health. While natural phytoremediation and clean-up measures of soils and water especially with respect to Fe, Zn and Pb be initiated in the study area.

References

1. Bankole, P. O. Information on Nigeria Environmental Profile, Federal Ministry of Environment, Mainframe publishers, Nigeria, 2005.
2. Adewole, M. B. and Uchegbu, L. U. Properties of Soils and Plants Uptake within the Vicinity of Selected Automobile Workshops in Ile-Ife, South-Western Nigeria. Ethiopian Journal of Environmental Studies and Management, 2010, 3(3).
3. Pam, A. A., Sha'Ato, R. and Offem, J. O. Contributions of Automobile Mechanic Sites to heavy Metals in Soil: A Case Study of North Bank Mechanic Village Makurdi, Benue State, Central Nigeria. Journal of Chemical, Biological and Physical Sciences, 2013, 3 (3): 2337 - 2347.
4. Utang, P, B., Ehidogin, O. S. and Ijekeye, C. L. Impacts of Automobile Workshops on Heavy Metals Concentrations of Urban Soils of Obio/Akpor LGA, Rivers State, Nigeria. African Journal of Agricultural Research, 2013, 8(26): 3476-3482.
5. Nwachukwu, M. A., Feng, H. and Achilike, K. Integrated Study of Automobile Wastes Management and Environmentally Friendly Mechanic Villages in Imo River Basin, Nigeria, African Journal of Environmental Science and Technology, 2010, 4(4): 234 - 249.

6. Wakawa, R. J., Uzairu, A., Kagbu, J. A. and Balarabe, M. L. Impact Assessment of Effluent Discharge on Physico-chemical Parameters and some Heavy Metal Concentrations in Surface Water of River Challawa, Kano, Nigeria. African Journal of Pure and Applied Chemistry, 2008, 2 (10): 100 - 106.
7. Sonawane, N. S., Sawant, C. P. and Patil, R. V. Soil Quality and Heavy Metal Contamination in Agricultural Soil in and around Toronmal (Triable Region) of Maharashtra, Archives of Applied Science Research, 2013, 5(2), 294-298.
8. Ekpo, F. E., Agu, N, N. and Udoakpan, U. I. Influence of Heavy Metals Concentrations in Three Common Fish, Sediment and Water Collected within Quarry Environment, Akamkpa LG Area, Cross Rivers State, Nigeria, European Journal of Toxicological Sciences, 2013, 3.
9. Omalu, I. C. J., Jibrin, A., Olayemi, I. K., Hassan, S. C., Mgbemena, C., Mgbemena, A. and Adeneran, L. A. Seroprevalence of malaria and Hepatitis B (HBsAg) with Associated Risk Factors among Pregnant Women attending Anti-natal Clinic in General Hospital Minna, North Central Nigeria. Annual Review and Research in Biology, 2012, 2(4): 83-88.
10. Najib, N. A., Mohammad, S. A., Ismail, S. H. and Wan-Ahmad, W. A. Assessment of Heavy Metal in Soil due to Human Activities in Kangar, Perlis, Malaysia International Journal of Civil and Environmental Engineering, 2012, 12(6): 28-34.
11. Olayinka, O. O. and Adedeji, O. H. Concentration of Heavy Metals in Soils near some Mechanic Villages in Abeokuta Metropolis, Ogun State, Nigeria. Journal of Advances in Chemistry, 2014, 8(3): 1667-1679.
12. Salano, E. M. Assessment of Heavy Metal Pollution in Soils and water of Samburu County, Kenya, Masters' Thesis, 2013, Kenyatta University, Kenya Retrieved From http://www.google.com/Heavymetalsinwater/salanoerick on May 22, 2014.
13. Akilu, A. Heavy Metals Concentration in Tannery Effluents, Associated Surface Water and soil at Ejersa Area of East Shoa, Ethiopia. Merit Research Journals of Environmental Science and Toxicology, 2013, 1(8): 156 - 163.
14. Mamtaz, R. and Chowdhury, H. Leaching characteristics of solid waste at an urban solid waste dumping site, Journal of Civil Engineering, 2006, 34: 71 - 79.
15. Zauro, S. A., Dabai, M. U., Tsafe, A. I., Umar, K. J. and Lawal, A. M. Extent of some Heavy Metals Contamination in Soil of Farmlands Around Sokoto Metropolis. European Scientific Journal, 2013, 9(3): 30-37.
16. Adewoyin, O. A, Hassan, A. T and Aladesida, A. A. The Impacts of Auto-Mechanic Workshops on Soil and Groundwater in Ibadan Metropolis, Global Journal of Environmental Science and Technology, 2013, 1(1): 57-64.
17. Okoro, A. C., Chukwuma, E. C., Nwachukwu, P. C. & Ezeh, K. A. Investigating the Effects of selected Heavy Metals on Topsoil at the Vicinities of Two Automobile Mechanic Villages, Owerri Municipal, Nigeria. The International Journal of Engineering and Sciences, 2013, 2(11): 19 - 26.
18. Shakery, A., Moor, F.and Razikordmahalleh, L.. Distribution of Soil Heavy Metal Contamination around Industrial Complex Zone, Shiraz, Iran, 19th World Congress of Soil Science Solutions for a Changing World, 2010, Brisbane, Australia.
19. Iyaka, Y. A. and Kakulu, S. E. Lead, Copper and Zinc Concentrations in Roadside Topsoil of Niger State, Nigeria, Journal of Emerging Trends in Engineering and Applied Sciences, 2011, 2 (5): 754 - 758.